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Efficient Catalytic Conversion of Dinitrogen to $N(SiMe_3)_3$ Using a Homogeneous Mononuclear Cobalt Complex

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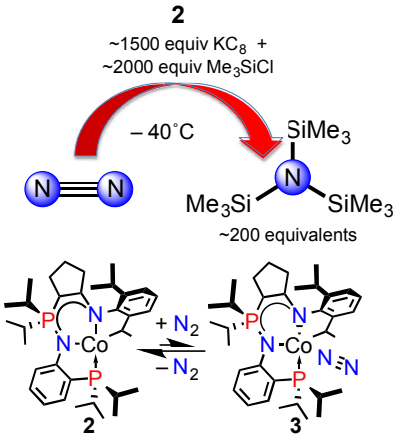


Supporting Information

ABSTRACT: Incorporation of the tridentate phosphine-enamidoiminophosphorane onto cobalt(II) produces tetrahedral Co(NpNP^{iPr})Cl, **1**, which upon reduction under dinitrogen generates the T-shaped, paramagnetic Co(I) complex Co(NpNP^{iPr}), **2**. This paramagnetic T-shaped derivative is in equilibrium with the paramagnetic dinitrogen derivative, Co(NpNP^{iPr})(N_2), **3**, which can be detected by IR and low temperature UV-vis spectroscopy. Both **1** and **2** act as a homogenous catalysts for the conversion of molecular nitrogen into tris(trimethylsilyl)amine ($N(SiMe_3)_3$) (~200 equiv, quantified as NH_4Cl after hydrolysis) in the presence of excess KC_8 and Me_3SiCl at low temperatures.

KEYWORDS. Dinitrogen, cobalt, ligand design, homogeneous catalysis, tris(trimethylsilylamine).

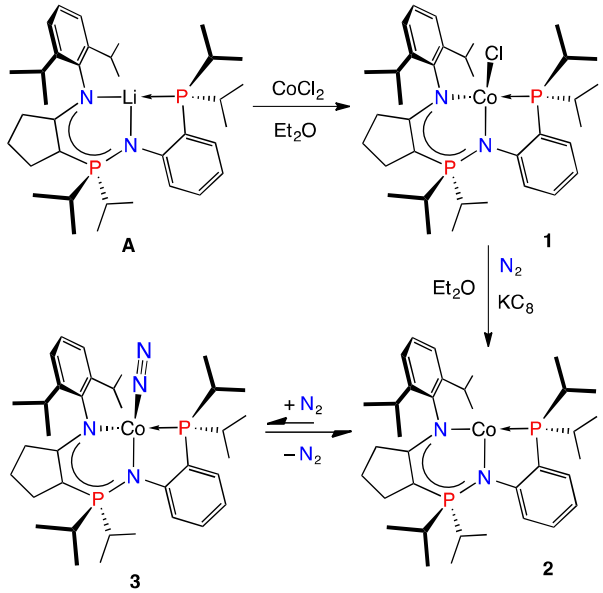
The only known industrial process that uses molecular nitrogen (N_2) as a feedstock is the Haber-Bosch reaction, which converts N_2 and dihydrogen (H_2) into ammonia (NH_3). The production of NH_3 by this process occurs at high pressures and temperatures over a heterogeneous iron or ruthenium catalyst, and since its discovery over 100 years ago, the major improvements have been to make this conversion more efficient.[1] While one can imagine many other transformations that could use N_2 as a feedstock,[2] the fact that no other process has been developed is likely due to the intrinsic inertness of this readily available diatomic molecule. Without a doubt the discovery of a new catalytic process that utilizes N_2 as reactant is a worthy goal and is being actively pursued by numerous research groups.[3]

Recently, some intriguing proof-of-concept homogeneous catalytic processes that use dinitrogen have been reported.[4] While not industrially relevant, the production of ammonia and hydrazine via the addition of excess reducing agents and proton sources to molecular nitrogen in the presence of various Mo, Fe, and Co complexes has generated many intriguing results. Interestingly, the very first report of a homogeneous process that was shown to convert N_2 to the higher value tris(trimethylsilyl)amine, $N(SiMe_3)_3$, actually predates the aforementioned ammonia-producing systems.[5] The conditions used for the catalytic production of $N(SiMe_3)_3$ also involve the reaction of N_2 in the presence of excess reducing agent, but with excess Me_3SiCl in lieu of protons. While the initial metal halide catalysts gave very low turnovers,[5a] the use of the Mo(0) dinitrogen-phosphine complex, *cis*-$Mo(N_2)_2(PMe_2Ph)_4$, gave 24 equivalents of $N(SiMe_3)_3$ per Mo center.[5b] More recent improvements on this catalytic process involve the use of a chelating diphosphine with a ferrocenyl backbone attached to generate a molybdenum dinitrogen complex, which produced 226 equiv of $N(SiMe_3)_3$;[6] even more intriguing, the use of a dicobalt system with a ligand scaffold that involves three amido units linked to three phosphine arms produced 196 equiv $N(SiMe_3)_3$ per Co_2 complex using similar reagents.[7] There are also mononuclear and polynuclear iron-based catalyst precursors and other metal systems that are productive in this reaction but generate lower numbers of equivalents

of tris(trimethylsilyl)amine (≤ 65 equiv/metal center).[8] To continue the advances in the area of catalytic dinitrogen conversion to higher value organonitrogen derivatives, exploration of chemical space to discover new productive systems is critical. In this work, we document an electron-rich iminophosphorane-cobalt derivative that acts extremely efficiently to produce $N(SiMe_3)_3$ (~200 equiv) via the reduction of N_2 in the presence of excess reducing agent and Me_3SiCl.

We have previously reported[9a] the synthesis of a new tridentate ligand precursor, Li(NpNP^{iPr}) (**A**) (where NpNP^{iPr} = phosphine-enamidoiminophosphorane); this ligand contains a Nacnac mimic[10] decorated with an electron-rich phosphine arm. Upon reaction of **A** with $CoCl_2$ in Et_2O, the cobalt(II) complex Co(NpNP^{iPr})Cl (**1**) is formed as shown in Scheme 1; **1** is isolated as brown crystals and is paramagnetic with μ_{eff} = 4.04 μ_B consistent with 3 unpaired electrons (S = 3/2, Evans method).

Scheme 1. Synthesis of Co(NpNP^{iPr})Cl (1) and reduction under N_2 to Co(NpNP^{iPr}) (2), which is in equilibrium with Co(NpNP^{iPr})(N_2) (3)



Reduction of **1** with potassium graphite (KC_8) in Et_2O under dinitrogen leads to the formation of **2**, which can be isolated as red crystals. In solution, under argon, **2** is also paramagnetic with μ_{eff} = 2.40 ± 0.05 μ_B, which is invariant from 293-193 K and corresponds to two unpaired electrons (S = 1).[11] Interestingly, as shown in Scheme 1, **2** exists in equilibrium with a small amount of the dinitrogen complex **3** (*vide infra*).

That the N_2 complex **3** forms to a small extent under dinitrogen was first evident upon taking an IR spectrum of the crystals of **2**, which revealed a weak absorption at 2071 cm^{-1}; performing the synthesis under $^{15}N_2$ resulted in a new band shifted to 2001 cm^{-1}. Re-examination of the solid-state structural data did show some residual electron density above the plane of the complex consistent with a small contamination of the crystals of **2** with dinitrogen complex **3**. Fortunately, after many attempts to grow crystals, we were able to isolate one batch that could be modeled by a 90:10 disorder in **2** with **3**.[12, 14] The individual structures are shown in Figures 1 and 2.

To provide further evidence for this equilibrium, we examined the solution UV-Vis spectrum of **2** under N_2 and observed changes as a function of temperature attributable to the formation of **3**: an absorption at 500 nm decreases as a function of temperature under N_2 whereas this same band shows no change under Ar when the temperature is lowered.[14]

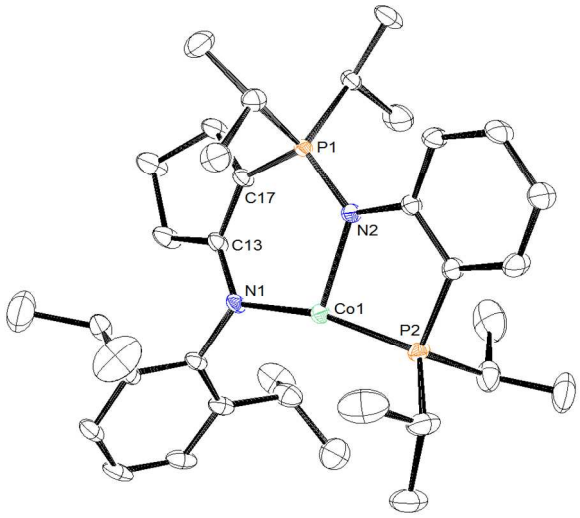


Figure 1. ORTEP drawing of the solid-state molecular structure of Co(NpNP^{iPr}) **2** (ellipsoids at 30% probability level), which is modeled as 90% of the disorder. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (deg): Co1–P2 2.1560(8), Co1–N1 1.9169(19), Co1–N2 2.028(2), P1–N2 1.630(6), P1–C17 1.753(2), N1–C13 1.337(4), C13–C17 1.389(4); N1–Co1–P2 166.13(8), P2–Co1–N2 87.20(7), N1–Co1–N2 106.34(10).

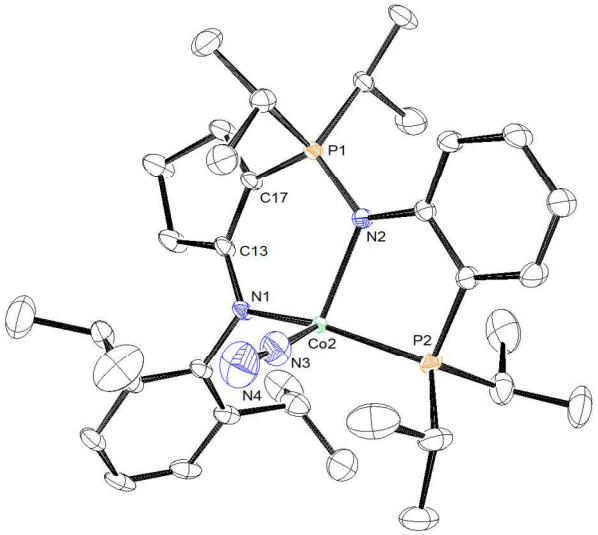


Figure 2. ORTEP drawing of the solid-state molecular structure of Co(NpNP^{iPr})N$_2$ **3** (ellipsoids at 30% probability level), which is modeled as a 10% disorder in **2**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (deg): Co2–P2 2.1851(7), Co2–N1 1.9735(19), Co2–N2 2.063(3), Co2–N3 1.99(4), N3–N4 1.12(6), P2–Co2–N1 152.91(7), P2–Co2–N2 85.57(6), P2–Co2–N3 91.6(9), N1–Co1–N2 106.34(10).

In solution (THF or toluene), we calculate via UV-vis spectroscopy (Figure 3) that at room temperature and 1 atm N_2, only about 15% of **3** is present at equilibrium, whereas at -80 ˚C, the mixture contains almost 90% of the dinitrogen complex **3**. Interestingly, ^{1}H NMR spectroscopy is not sensitive to the formation of **3** as the variable temperature NMR spectra of **2** under Ar and **2** under N_2 do not show any differences as a function of temperature (293 K – 193 K)[14]. In contrast, the related T-shaped Co(I) complex, Co(^{Si}PNP) (where (^{Si}PNP) = N(SiMe$_2$CH$_2$PBu$^t_2$)$_2$), is in equilibrium with the *diamagnetic square planar* dinitrogen complex Co(^{Si}PNP)(N$_2$);[13a] other Co(PNP) systems typically generate diamagnetic N_2 complexes upon reduction under dinitrogen.[4d, 13e]

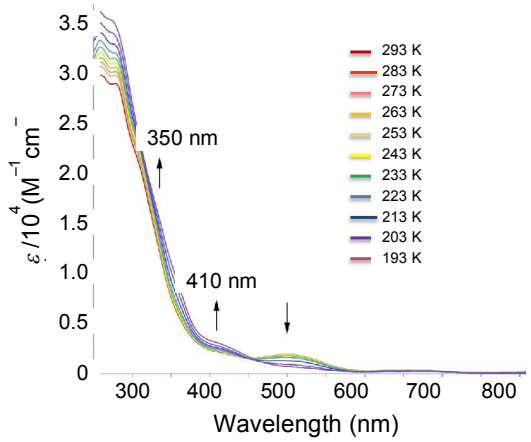
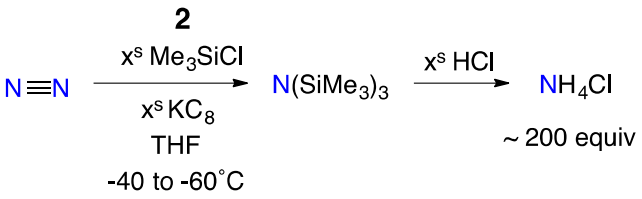


Figure 3. UV-vis spectra of **2** in toluene under N_2 as a function of temperature.

On the basis of the above solution spectral data, the structure of **3** is distorted tetrahedral, which was confirmed by the disordered solid-state structure of **2** (Figures 1 and 2).[13] Additional support for the presence of the tetrahedral paramagnetic dinitrogen complex **3** is that the IR stretching frequency of the coordinated N_2 unit of 2071 cm^{-1} is indicative of very weak activation of the dinitrogen moiety, which contrasts the corresponding IR stretching frequency of the aforementioned Co(^{Si}PNP)(N$_2$) at 2004 cm^{-1}; this lower stretching frequency is consistent with a low spin Co(I) complex[13a] and more back bonding from Co to the N_2 unit. The two-coordinate iron(0) complex, Fe(CAAC)$_2$ (where CAAC = bulky cyclic(amino)-alkyl(carbene)), also coordinates dinitrogen only at low temperatures (<-80 ˚C), which facilitates isolation of the anionic dinitrogen complex, [Fe(CAAC)$_2$N$_2$]$^-$, upon reduction at low temperature with KC_8 in the presence of [18-crown-6]. Importantly, Fe(CAAC)$_2$ is productive in the catalytic silylation of N_2 to produce 20 – 27 equiv of N(SiMe$_3$)$_3$ using excess KC_8 (600 equiv) and Me$_3$SiCl (600 equiv) at room temperature.[8c]

We investigated the ability of the T-shaped Co(I) complex **2** to act as a catalyst precursor for the catalytic silylation of dinitrogen. The general conditions are shown in Scheme 2.

Scheme 2. Conditions: 1 atm N_2, ~2000 equiv Me$_3$SiCl and ~1500 equiv KC_8 with respect to 1 equiv of 2.



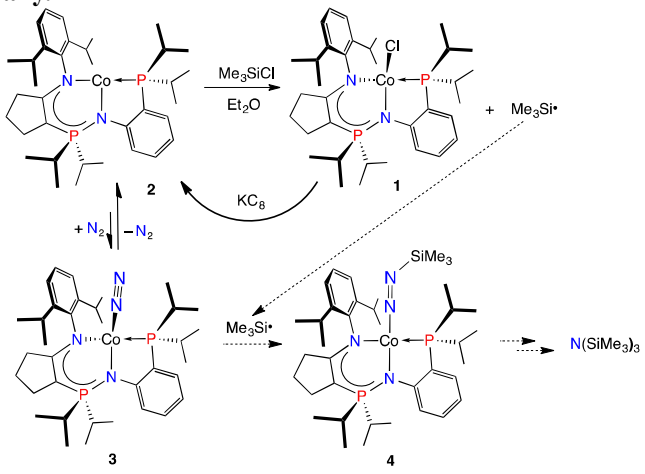
Optimization experiments showed that low temperatures and long reaction times (10 days) favored highest turnover numbers; in fact, at -40 ˚C, we observed 200 ± 20 equivalents of N(SiMe$_3$)$_3$ with **2** as the catalyst precursor using excess reducing agent (KC_8) and Me$_3$SiCl; analysis was carried after hydrolysis with excess HCl.[14, 15] The conditions indicated in the caption to Scheme 2 were done in triplicate and vary by ± 10%. The more efficient catalytic turnover at low temperature is consistent with the aforementioned shift in the equilibrium favoring formation of the N_2 complex **3**. We also find that the choice of solvent is important; THF and DME generate similar efficient turnovers while toluene is inferior.[14] We also tested catalyst robustness; after 10 days (215 equiv N(SiMe$_3$)$_3$ measured after hydrolysis), the solution was filtered and a new charge of 2000 equiv Me$_3$SiCl and 1500 equiv KC_8 was added and the mixture stirred for 3 days at -40 ˚C. This generated an additional 55 equiv of N(SiMe$_3$)$_3$ after hydrolysis (total = 270 equiv).

We have endeavored to understand this process by performing a number of preliminary stoichiometric reactions. For example, addition of Me$_3$SiCl to the T-shaped Co(I) complex Co(NpNP^{iPr}) (**2**) partially regenerates[14] the starting Co(II) species Co(NpNP^{iPr})Cl (**1**) as shown at the top of Scheme 3. The fate of the Me$_3$Si• radical is unknown, but we suggest that it can react with the small amount of dinitrogen complex **3** present at low temperature to generate putative Co(NpNP^{iPr})(NNSiMe$_3$) (**4**), a likely intermediate[6,7,13] in the formation of tris(trimethylsilyl)amine. Unfortunately, our attempts to detect this species or other intermediates have thus far been unsuccessful.

One intriguing idea (Scheme 3) is that the equilibrium between T-shaped **2** and dinitrogen complex **3** may con-

tribute to how this system catalytically turns over: coordinatively unsaturated **2** abstracts Cl• from Me_3SiCl to generate the Co(II) chloride **1**, which is then reduced by the excess KC_8 back to **2**; dinitrogen complex **3** traps the generated Me_3Si•. Consistent with this is that starting Co(II) chloride complex **1** acts as an efficient catalyst for this reaction under these conditions with comparable turnover numbers for $N(SiMe_3)_3$ generation.[14] Separate attempts to generate another potential species in the process, the anionic formally Co(0) dinitrogen complex $K[Co(NpNP^{iPr})N_2]$, by subjecting **2** to excess KC_8 in the presence of N_2 have been inconclusive at this point. Such stoichiometric reactions are continuing.

Scheme 3. Proposal for the formation of $N(SiMe_3)_3$; the intermediate 4 has been confirmed computationally.[14]



In conclusion, the results of this study broaden the scope of potential catalyst systems for dinitrogen activation by including an iminophosphorane-based ligand system that generates a mononuclear cobalt complex, which has been shown to be extremely effective in the homogenous catalytic functionalization of molecular nitrogen to generate $N(SiMe_3)_3$. One possible rationale for the efficacy of this system may be that the iminophosphorane ligand framework is sufficiently bulky and only mildly basic, both of which allow the catalyst to survive under the strongly reducing conditions of this process. What is also important is that we provide another example of a weakly bound terminal N_2 moiety that can participate in processes that result in functionalization of N_2.[8c] More mechanistic studies are in progress as well as iterative ligand designs to examine the dependence of turnover numbers to structural changes and probe the equilibrium between analogues of **2** and **3**. Future work will also explore more atom-economic ways to generate silyl radicals, for example photochemical cleavage of disilanes and photo-induced demetallation of $M(SiR_3)_2$ type species.[16]

ASSOCIATED CONTENT

Supporting Information. Supporting Information is available free of charge on the ACS Publications Website at DOI: 10.1021/acscatal.XXXXX.

Experimental Details, solution and solid-state characterization of compounds, DFT studies, details of catalysis experiments (PDF)

X-ray data (CIF)

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Author Contributions

The manuscript was written through contributions of all authors.

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(13) Co[^{Si}PNP] = Co[$N(SiMe_2CH_2P^tBu_2)_2$] reported in (a) Ingleson, M.; Fan, H.; Pink, M.; Tomaszewski, J.; Caulton, K. G. Three Coordinate Co(I) Provides Access to Unsaturated Dihydrido-Co(III) and Seven-coordinate Co(IV). *J. Am. Chem. Soc.* **2006**, *128*, 1804 – 1805; (b) Ingleson, M. J.; Pink, M.; Fan, H.; Caulton, K. G. Exploring the Reactivity of Four-coordinate PNPCoX with Access to Three-coordinate Spin Triplet PNPCo. *Inorg. Chem*. **2007**, *46*, 10321 – 10334; (c) Ingleson, M. J.; Pink, M.; Fan, H.; Caulton, K. G. Redox Chemistry of the Triplet Complex (PNP)CoI. *J. Am. Chem. Soc.* **2008**, *128*, 4262 – 4276; for the related carbon backbone Co[PNP], where PNP = $N(CH_2CH_2PPr^i_2)_2$, see (d) Rozenel, S. S.; Padilla, R.; Camp C.; Arnold, J. Unusual Activation of H_2 by Reduced Cobalt Complexes Supported by a PNP Pincer Ligand. *Chem. Commun.,* **2014**, *50*, 2612 – 2614.; (e) Rozenel, S. S. ; Padilla, R. M.; Arnold, J. Chemistry of Reduced Monomeric and Dimeric Cobalt Complexes Supported by a PNP Pincer Ligand. *Inorg. Chem*., **2013**, *52*, 11544 – 11550.

(14) See Supporting Information for analytical procedures, synthesis details, optimization experiments, computational methods and results, and detailed product analyses.

(15) There are a number of different protocols for determining the yield of $N(SiMe_3)_3$ in this catalytic reaction; while some measure the amount of $N(SiMe_3)_3$ directly by GC-MS,[6,7] others hydrolyze with excess HCl to generate NH_4Cl and either analyze by the indophenol

method or by ^{1}H NMR spectroscopy using an internal standard.[8a,b] We have used all of these methods but report the indophenol method in the Supporting Information. In certain experiments we have found the GC-MS method to give slightly lower turnovers of $N(SiMe_3)_3$.

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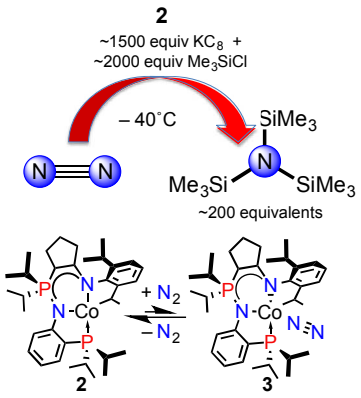
2
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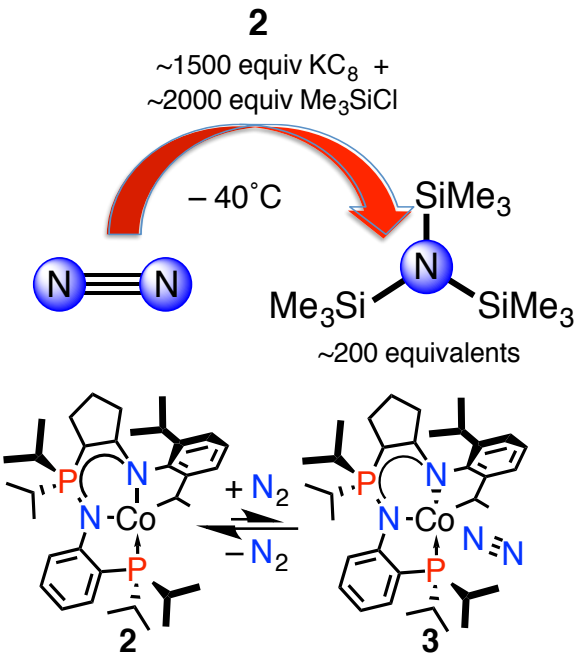
~2000 equiv Me3SiCl
– 40˚C
SiMe3
N
N
Me3Si
SiMe3
~200 equivalents
P
N
N-Co
P
+ N2
– N2
2
3


2
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~2000 equiv Me3SiCl
– 40˚C
SiMe3
N
N
N
Me3Si
SiMe3
~200 equivalents
P
N
N-Co
P
+ N2
– N2
2
P
N
N-Co
N≡N
P
3